## Heterocycles

# Arsenic-Mediated C–C Coupling of Cyanides Leading to Cyanido Arsazolide $[AsC_4N_4]^-$

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**Abstract:** The chemistry of arsenic cyanides has been investigated and is found to be completely different to the chemistry of the heavier analogs antimony and bismuth as well as phosphorus. The reaction of As(CN)<sub>3</sub> with cyanide salts resulted in the formation of an unknown cyanido arsazolide heterocycle, which represents a structure isomer of the desired [As(CN)<sub>4</sub>]<sup>-</sup>. The structure, bonding, and formation of this unusual heterocycle is discussed featuring an arsenic mediated C–C coupling of cyanides. [AsC<sub>4</sub>N<sub>4</sub>]<sup>-</sup> salts with different counterions such as [PPh<sub>4</sub>]<sup>+</sup>, [PPN]<sup>+</sup> = [Ph<sub>3</sub>P-*N*-PPh<sub>3</sub>]<sup>+</sup>, Ag<sup>+</sup>, and [BMIm]<sup>+</sup> are reported with [BMIm][AsC<sub>4</sub>N<sub>4</sub>] being a low-temperature ionic liquid ( $T_m = -62$  °C).

Whereas the isolation and full characterization of all heavy pnictogen tricyanides,  $E(CN)_3$  (E = P–B),<sup>[1–8]</sup> were reported, ternary cyanidopnictate anions have been known so far only for phosphorus,<sup>[9–12]</sup> antimony,<sup>[13]</sup> and bismuth<sup>[13]</sup> but not for arsenic (Schemes 1 and 2). Herein, we communicate the unusual C–C coupling of cyanides mediated by arsenic upon the attempt-



Scheme 1. Isolated heavy ternary cyanido pnictogen anions.

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(i)  $E(CN)_3 + n$  [Cat]CN (ii)  $EX_3 + n$  [Cat]CN + 3 Me<sub>3</sub>SiCN (Cat]<sub>n</sub>[ $E(CN)_{3+n}$ ] + 3 Me<sub>3</sub>SiX

Scheme 2. Synthesis of salts containing  $[E(CN)_{3+n}]^{n-}$  ions (X=F, Cl; n = 1-3;  $[Cat]^+ = [PPh_4]^+$ ,  $[PPN]^+ = [Ph_3P-N-PPh_3]^+$ ; solvent = excess Me<sub>3</sub>SiCN, CH<sub>3</sub>CN, ionic liquids).

ed synthesis of cyanido arsenates of the type  $[As(CN)_{3+n}]^{n-}$ (n = 1, 2, 3), yielding an unprecedented cyanido arsazolide heterocycle (Scheme 3, Figure 1 right).



Scheme 3. Known 5-membered As/N-heterocycles. (Ter = 2,6-bis(2,4,6-trime-thylphenyl)phenyl, Dmp = 2,6-dimethylphenyl,  $Mes^* = 2,4,6$ -tri-*tert*-butyl-phenyl).

Two approaches to  $[E(CN)_{3+n}]^{n-}$  ions were reported so far: [11, 13] i) Starting from E(CN)<sub>3</sub> in the reaction with weakly coordinating cyanide salts of the type [Cat]CN ([Cat]<sup>+</sup> = for example,  $[PPh_4]^+$ ,  $[PPN]^+ = [Ph_3P - N - PPh_3]^+$ ) and ii) treatment of EX<sub>3</sub> with [Cat]CN in the presence of molar amounts of Me<sub>3</sub>SiCN (X = halogen; Scheme 2). Interestingly, while  $[P(CN)_4]^-$  was described as a highly labile intermediate in the reaction of P(CN)<sub>3</sub> with CN<sup>-</sup> sources, quickly decomposing to give [NC-P-CN]<sup>-</sup> and the unusual  $[P_2C_{10}N_{10}]^{2-}$  (Scheme 1),  $^{[11]}$  the formation and isolation of the heavy cyanido pnictogen anions of the type  $[E(CN)_{3+n}]^{n-}$  (E=Sb, Bi) was only achieved when EX<sub>3</sub> was treated with cyanide salts and Me<sub>3</sub>SiCN (Schemes 1 and 2),<sup>[13]</sup> since  $E(CN)_3$  (E=Sb, Bi) are highly polymeric species that are almost insoluble in common organic solvents, so that no reaction was observed even after several days of reaction time and under reflux. So it was interesting to see how arsenic performs, either

1



**Figure 1.** Left) ORTEP representation of  $[As(CN)_3Cl_2]^{2-}$  (left, disorder not shown) and right)  $[AsC_4N_4]^-$  in the crystal. Thermal ellipsoids correspond to 50% probability at 173 K. [PPh<sub>4</sub>]<sup>+</sup> ions are omitted for clarity. Selected bond lengths [Å] and angles [°]:  $[As(CN)_3Cl_2]^{2-}$ : As1–C1 2.032(2), As1–C2 1.922(7), As1–C3 2.01(1), As1–Cl1 2.736(1), As1–Cl2 2.808(1), C1-As1-C2 87.4(1), C1-As1-C3 85.4(2), C2-As1-C3 89.8(4); Cl1-As1-Cl2 108.1(4).  $[AsC_4N_4]^-$ : As1–N1 1.801(2), As1–N2 1.803(2), N1–C1 1.334(2), N2–C2 1.340(2), C2–C4 1.439(2); N1-As1-N2 93.29(6), C1-N1-As1 106.7(1), N3-C3-C1 177.5(2), N4-C4-C2 179.4(2).

similar to phosphorus with no stable  $[E(CN)_{3+n}]^{n-}$  salts or like the heavier antimony and bismuth that do form stable salts bearing  $[E(CN)_{3+n}]^{n-}$  ions.

In a first series of experiments, AsCl<sub>3</sub> was treated with different cyanide sources such as [PPh<sub>4</sub>]CN or KCN in Me<sub>3</sub>SiCN or mixtures with acetonitrile at ambient temperatures as well as slightly elevated temperatures (Scheme 2, path ii). The only product that could be isolated in moderate yields (36%) was [PPh<sub>4</sub>]<sub>2</sub>[As(CN)<sub>3</sub>Cl<sub>2</sub>] (Figure 1, left), but in no case complete Cl<sup>-/</sup> CN<sup>-</sup> substitution was observed. The solid state structure of [PPh<sub>4</sub>]<sub>2</sub>[As(CN)<sub>3</sub>Cl<sub>2</sub>] (Figure 1, left) contains well-separated cations and monomeric anions, which display a sterically active lone pair and a monomeric square-based pyramidal (pseudo-octahedral) structure that is strongly distorted (Cl1-As1-Cl2 108.1(4)°, C1-As1-C3 85.4(2)°).

To avoid the Cl<sup>-</sup>/CN<sup>-</sup> substitution problem (see below) we started from As(CN)<sub>3</sub> (reaction i, Scheme 2) in a second series of experiments. Regardless of the stoichiometry, cyanide source, and solvent (e.g., CH<sub>3</sub>CN, Me<sub>3</sub>SiCN, or even ionic liquids such as [BMIm][OTf],  $OTf = F_3 CSO_2 O^-$ ) we used, we were never capable of isolating any cyanide arsenate of the type [As- $(CN)_{3+n}]^{n-}$ , but always a structure isomer of  $[As(CN)_4]^-$ , the 4,5dicyano-1,3,2-diazarsolide [AsC<sub>4</sub>N<sub>4</sub>]<sup>-</sup> (Figure 1, right) in rather good yields (up to 70%). The best yields were obtained with [PPN]<sup>+</sup> as counterion and a slight excess of [PPN]CN in the reaction with As(CN)<sub>3</sub> (1:1.25) in acetonitrile at ambient temperatures (Scheme 2, reaction i). The presence of the  $[AsC_4N_4]^-$  heterocycle was unequivocally proven by single-crystal X-ray studies on different salts ([PPN]<sup>+</sup>, [PPh<sub>4</sub>]<sup>+</sup>, [Ag(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>) containing this heterocycle (Figure 1 and Tables S1-S6 in the Supporting Information).

With the [PPN][AsC<sub>4</sub>N<sub>4</sub>] in hand, we were able to substitute the weakly coordinating cation [PPN]<sup>+</sup> by Ag<sup>+</sup> in the reaction with AgNO<sub>3</sub> in CH<sub>3</sub>CN in 95% yield. The silver salt turned out to be hardly soluble in most common solvents. Even in dimethyl sulfoxide, the solubility was very low. Solvates of the silver salt were obtained upon dissolving small amounts and recrystallization in DMSO or adding PPh<sub>3</sub>, which significantly increases the solubility of the silver salt in CH<sub>3</sub>CN (Figure 2, Scheme S3 and Table S5 in the Supporting Information). Of special interest might be the 1-butyl-3-methylimidazolium salt [BMIm][AsC<sub>4</sub>N<sub>4</sub>] that was afforded by treating Ag[AsC<sub>4</sub>N<sub>4</sub>] with



Figure 2. Left) Section of a chain in  $[Ag(PPh_3)_2][AsC_4N_4]$  and right) view along the threefold rotational axis of the helix (Ph groups omitted for clarity).

[BMIm]Cl (83% yield). While all other here described salts decompose (without melting) above 140° ([PPh<sub>4</sub>]<sup>+</sup>: 144°C; [PPN]<sup>+</sup>: 151°C; Ag<sup>+</sup>: 159°C; [Ag(PPh<sub>3</sub>)]<sup>+</sup>: 183°C), [BMIm] [AsC<sub>4</sub>N<sub>4</sub>] melts as low as -62°C, thus representing a low-temperature ionic liquid due to a very good charge delocalization (see below). All these [AsC<sub>4</sub>N<sub>4</sub>]<sup>-</sup> salts can be prepared in bulk, are only slightly moisture and air sensitive, but long termstable under argon. These properties allow follow-up chemistry and thus render these salts a valuable starting material.

Single-crystal X-ray studies of all salts containing [AsC<sub>4</sub>N<sub>4</sub>]<sup>-</sup> revealed a planar 5-membered heterocycle with rather short As–N (between 1.77–1.84, cf.  $\Sigma r_{cov}(As = N) = 1.74 \text{ Å})^{[14]}$  and  $C_{ring}$ -N<sub>ring</sub> distances (1.31–1.37,  $\Sigma r_{cov}(C=N) = 1.27$  Å)<sup>[14]</sup> featuring partial double bond character. The first compound with an As= N double bond (d(As-N) = 1.714(7) and 1.745(7) Å) was N,N'bis(2,4,6-tri-tert-butylphenyl)amino-iminoarsane, prepared by Lappert et al. in 1986.<sup>[15]</sup> While a few cationic diazarsenium<sup>[16-18]</sup>  $(\mathbf{A}^{[16]} d(\text{As}-\text{N}) = 1.763, \mathbf{B}^{[19]} 1.803 - 1.814 \text{ Å})$  and neutral tetrazaarsole  $(d(As-N) = 1.784 - 1.805 \text{ Å})^{[20]}$  heterocycles are known (Scheme 3, species A-C), anionic diazarsolides are hitherto unknown. Only recently, neutral triazarsole heterocycles were isolated either by insertion of isonitriles into arsatriazanediyls  $[As(\mu-NTer)_2N]$ (Ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl,  $D d(As-N) = 1.875 \text{ Å})^{[21]}$  and by making use of a [3+2] cycloaddition reaction between an arsaalkyne and an organic azide (species **E** d(As-N) = 1.839 Å).<sup>[22]</sup> Arsolides of the type  $[R_4C_4As]^-$ (R=Ph, Et) were described by Westerhausen et al.<sup>[23,24]</sup> Neutral group 16 analogues of  $[AsC_4N_4]^-$  were obtained in the reaction of 2,3-diaminomaleonitrile with ECl<sub>4</sub> (E=Se, Te) in the presence of organic bases.<sup>[25-27]</sup>

Interestingly, while the solid state structures of  $[Cat][AsC_4N_4]$ ( $[Cat] = [PPN] = [PPh_4]$ ) contain well-separated cations and monomeric anions, all silver salts display coordination polymers, for example, the most prominent structural feature in  $[Ag(PPh_3)_2][AsC_4N_4]$  represents a chain with a threefold rotational axis (Figure 2) with a tetrahedrally coordinated Ag<sup>+</sup> ion connecting two adjacent  $[AsC_4N_4]^-$  ions via the ring N atoms in

2



addition to coordination to two  $PPh_3$  molecules. The exocyclic CN groups of  $[AsC_4N_4]^-$  ions remain uncoordinated.

Finally, DFT, NBO, and NRT computations at the pbe/aug-ccpvdz level (see the Supporting Information, DFT = density functional theory, NBO = natural bond theory, NRT = natural resonance theory) were carried out to shed light into the bonding and formation of  $[AsC_4N_4]^-$ . Solvent effects, which are essential to stabilize charged ions, are incorporated using the integral equation formalism version of the polarizable continuum model (PCM, solvent = acetonitrile). The frontier orbitals display the characteristic features of aromatics and a strong coupling of the  $6\pi$ -electron 5-membered ring with the two CN groups leading to a formal  $10\pi$ -electron-9-center bonding system (Table S7 in the Supporting Information). The LUMO and HOMO are strongly localized on the arsenic atom. In accord with these MO considerations, NBO/NRT analyses show resonance between Lewis representations exhibiting delocalization of the  $6\pi$  electrons (Scheme 4). In accord with this, NBO occupation of p atomic orbitals perpendicular to the five-membered ring amounts to 5.8 e (As 1.05,  $N_{\text{ring}}$  1.28,  $C_{\text{ring}}$  1.09 e). This situation resembles the situation in nonlinear resonancestabilized pseudohalides such as tetracyanopyrrolides.<sup>[28]</sup>

Finally, we want to answer the question how  $[AsC_4N_4]^-$  is formed from its structural isomer  $[As(CN)_4]^-$  (2), which can be assumed to be formed in the first reaction step when  $As(CN)_3$ (1) is treated with  $CN^-$  (Scheme 5). The barrier-free formation of  $[As(CN)_4]^-$  was computed to be slightly exergonic (-9.3 kcal mol<sup>-1</sup>), while the addition of a second  $CN^-$  ion and formation of  $[As(CN)_5]^{2-}$  (3) represents a slightly endergonic process (+1.3 kcalmol<sup>-1</sup>). The transient formation of  $[P(CN)_4]^-$  in the analogous reaction was proven by <sup>31</sup>P NMR experiments.<sup>[11]</sup> Such NMR experiments with  $^{75}$ As (I = 3/2) are not feasible due to the quadrupole moment. The crucial step with the largest activation barrier (TS1 22.8 kcal mol<sup>-1</sup>) is the attack of one CN<sup>-</sup> ligand at the carbon atom of an adjacent CN<sup>-</sup> ligand, leading to the formation of dicyanidoarsenide [As(CN)<sub>2</sub>]<sup>-</sup> and cyanogen (NC-CN). Note, the attack of free CN<sup>-</sup> at one carbon atom of  $[As(CN)_4]^-$  does not work as in this case always  $[As(CN)_5]^{2-}$  is formed in a barrier-free process. Once cyanogen is formed, all other barriers are smaller and the reaction proceeds rather fast to  $[AsC_4N_4]^-$  (5); free  $CN^-$  ions attack cyanogen thereby forming  $[(NC)_2C=N]^-$  (**TS2** 12.8 kcalmol<sup>-1</sup>). This reaction seems to be the reason why a slight access of CN<sup>-</sup> in the reaction mixture increases the yields. Actually, a similar reaction is known for the synthesis of diiminosuccinonitrile from HCN and cyanogen in the presence of Et<sub>3</sub>N. Here, the base deprotonates HCN forming CN<sup>-</sup>, which attacks cyanogen twice. However, protons are needed to form diiminosuccinonitrile. If no protons are available, for example, in the reaction of NC-CN with KCN, the authors describe the formation of a bicyclic  $[C_7N_7]^-$  ion. Since in our reaction setup [As(CN)<sub>2</sub>]<sup>-</sup> is present, [(NC)<sub>2</sub>C=N]<sup>-</sup> reacts in a barrier free  $S_N 2$  type substitution reaction to  $[(NC)As(NC)_2C=N)]^-$  (4) and one  $CN^-$  of  $[As(CN)_2]^-$  is eliminated.<sup>[29]</sup> Again free CN<sup>-</sup> can now attack one carbon atom of the  $[(NC)_2C=N]^-$  ligand in 4, affording transition state TS3, an open chain NCCN-As species with an activation barrier of 21.0 kcal  $mol^{-1}$ . Upon formation of the final  $[AsC_4N_4]^-$  heterocycle (5), the last remaining CN<sup>-</sup> ion in 4 is released. Interestingly, we could not find a local minimum for an open chain isomer of  $[AsC_4N_4]^-$  along this reaction path, which means that the attack of the  $CN^-$  ion at the  $[(NC)_2C=N]^-$  ligand in 4 leads directly to ring formation and elimination of CN<sup>-</sup>. The formation

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Scheme 4. Most important Lewis representations (out of 189) and their computed resonance weight (delocalization into CN triple bond omitted for clarity).



**Scheme 5.** Potential energy diagram for the formation of  $[AsC_4N_4]^-$  (5) starting from  $As(CN)_3$  using the pbe density functional with aug-cc-pvdz basis sets for C and N, and a ECP10MDF core potential for arsenic (see the Supporting Information, a = barrier free process, PCM method applied).

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Chem. Eur. J. 2017, 23, 1-5



of heterocycle  $[AsC_4N_4]^-$  (5) is energetically favored by 46.3 kcal  $mol^{-1}$  compared to its isomer  $[As(CN)_4]^-$  (2). It should be mentioned that the attack of  $CN^-$  at the free  $[(NC)_2C=N]^-$  yielding the  $[(NC)_2(C=N)_2]^{2-}$  ion is an endergonic process with 27.6 kcal  $mol^{-1}$  and a rather large activation barrier of 27.9 kcalmol<sup>-1</sup>, again indicating an arsenic mediated C-C coupling process. At last, we have computed the activation barriers for the heavier congeners  $[E(CN)_4]^-$ , which are significantly hiaher (TS1(Sb) 32.3 kcal mol<sup>-1</sup>, TS1(Bi) 34.0 kcal mol<sup>-1</sup>), nicely explaining why in these cases no isomerization to an heterocycle  $[EC_4N_4]^-$  was observed, but always the formation of  $[E(CN)_5]^{2-}$ , since here also the second CN<sup>-</sup> ion is bound in an exergonic process ( $[E(CN)_4]^- + CN^- \rightarrow [E(CN)_5]^{2-}$ ; E=Sb -3.2, Bi -5.3, cf.  $As + 1.3 \text{ kcal mol}^{-1}$ ).

In summary, we have demonstrated a facile synthetic access to the first cyanido arsazolide  $[AsC_4N_4]^-$  that has been fully characterized.  $[AsC_4N_4]^-$  is formed in an unusual isomerization process from its structural isomer [As(CN)<sub>4</sub>]<sup>-</sup>, which is formed first as a transient species when As(CN)<sub>3</sub> is treated with CN<sup>-</sup>. Then, two arsenic mediated C-C coupling steps occur, leading finally to the formation of the  $[AsC_4N_4]^-$  aromatic ring system, which can be considered a resonance-stabilized pseudohalide.

#### **Experimental Section**

Experimental and computational details can be found in the Supporting Information.

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#### **Conflict of interest**

The authors declare no conflict of interest.

Keywords: arsenic · C–C coupling · cyanides · isomerization · heterocycles

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# COMMUNICATION

**Go get some cyanide and...isomerize:** A novel  $[AsC_4N_4]^-$  heterocycle is formed in an unusual isomerization process from its structural isomer  $[As(CN)_4]^-$ , which is formed as transient species when  $As(CN)_3$  is treated with  $CN^-$  (see scheme). Two arsenic-mediated C–C coupling steps are necessary for the formation of the  $[AsC_4N_4]^-$  aromatic ring system.



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